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14. ABSTRACT
Fuels that can be ignited chemically under ambient conditions upon contact with an oxidizing agent are referred to as hypergols.[1] Engines powered by hypergols do not require electric ignition, making them simple, robust and reliable alternatives to conventional fossil fuels. Commonly used hypergolic fuels include hydrazine and its methylated derivatives, which are extremely toxic, corrosive, and have high vapor pressure. Intense research is underway to develop alternative environmentally friendly liquid propellants with lower toxicity to reduce operational costs and safety requirements associated with handling hydrazine.[2] Ionic liquids (ILs)[3] have recently received considerable attention as energetic materials for propellant applications due to lower vapor pressures, higher densities and, often, an enhanced thermal stability compared to their nonionic analogues.[4] Since 2008, a number of ILs have been reported to be hypergolic when reacted with common oxidizers, such as HNO_3.[5-7] Of particular practical interest are hypergolic ILs comprising fuel-rich dicyanamide (DCA) anions.[5] DCA ILs have some of the lowest viscosities among known ILs,[8] which is a very important figure of merit for the efficient fuel supply in bipropellant engines.

In this study, using electrospray ionization mass spectrometry (ESI-MS), we discovered that the reaction between DCA ILs and HNO_3 yields a precipitate that is composed of cyclic triazines, including melamine and its polymers. The concurrent formation of precipitate siphons materials from the hypergolic reaction pathway,[6] limiting the energy capacity of a fuel. Furthermore, the generation of stable solid-state species during the ignition indeed represents a serious problem for the safe operation of bipropellant engines. We propose a mechanism for the formation of the major polymers via thermal decomposition of DCA ILs, mediated by nitric acid. The reaction of DCA ILs with HNO_3 represents a new method to synthesize cyclic azines, which can be tuned by choosing various different IL precursors.

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Generation of Melamine Polymer Condensates upon Hypergolic Ignition of Dicyanamide Ionic Liquids

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Fuels that can be ignited chemically under ambient conditions -- upon contact with an oxidizing agent -- are referred to as hypergols.[1] Engines powered by hypergols do not require electric ignition, making them simple, robust and reliable alternatives to conventional fossil fuels. Commonly used hypergolic fuels include hydrazine and its methylated derivatives, which are extremely toxic, corrosive, and have high vapor pressure. Intense research is underway to develop alternative environmentally friendly liquid propellants with lower toxicity to reduce operational costs and safety requirements associated with handling hydrazine.[2] Ionic liquids (ILs)[3] have recently received considerable attention as energetic materials for propellant applications due to lower vapor pressures, higher densities and, often, an enhanced thermal stability compared to their nonionic analogues.[4] Since 2008, a number of ILs have been reported to be hypergolic when reacted with common oxidizers, such as HNO_3.[5-7] Of particular practical interest are hypergolic ILs comprising fuel-rich dicyanamide (DCA) anions.[5] DCA ILs have some of the lowest viscosities among known ILs,[8] which is a very important figure of merit for the efficient fuel supply in bipropellant engines.

In this study, using electrospray ionization mass spectrometry (ESI-MS), we discovered that the reaction between DCA ILs and HNO_3 yields a precipitate that is composed of cyclic triazines, including melamine and its polymers. The concurrent formation of precipitate siphons materials from the hypergolic reaction pathway,[6] limiting the energy capacity of a fuel. Furthermore, the generation of stable solid-state species during the ignition indeed represents a serious problem for the safe operation of bipropellant engines. We propose a mechanism for the formation of the major polymers via thermal decomposition of DCA ILs, mediated by nitric acid. The reaction of DCA ILs with HNO_3 represents a new method to synthesize cyclic azines, which can be tuned by choosing various different IL precursors.

The condensate was found to be very poorly soluble in water as well as in a set of organic solvents, including dichloromethane, acetonitrile, chloroform, m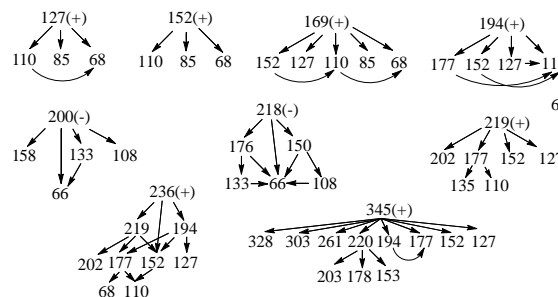ethanol, toluene, ethyl acetate, and diethyl ether. The solubility dramatically increased, however, in ammonium hydroxide (10% *vol*), suggesting the high content of nitrogen atoms in the species constituting the precipitate.

Figure 1 shows positive and negative ion mode mass spectra of the precipitate formed in the reaction between 1-butyl-3-methyl-imidazolium dicyanamide and white fuming HNO_3 (WFNA, ~ 100%) after dissolution in ammonium hydroxide. Note that all the peaks in Figure 1 were also observed from the liquid phase of the residue suspension in pure water without ammonia, although at a considerably lower intensity caused by its much reduced solubility. Consequently, we can exclude the possible origin of these peaks as a result of chemical reaction between the residue and ammonia.
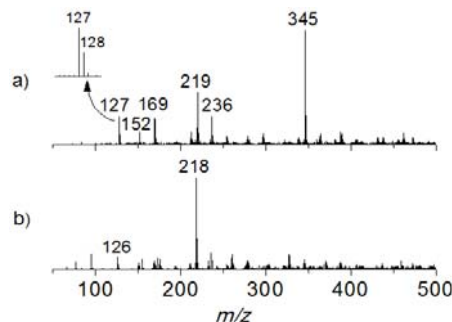
Figure 1. ESI-MS of the precipitate formed during the reaction between 1-butyl-3-methylimidazolium dicyanamide and WFNA. The precipitate was dissolved in an aqueous solution of ammonia (10% *vol*) and analyzed directly in positive (a) and negative (b) ion detection modes.

Scheme 1 summarizes the results of tandem MS analysis for each peak. We observe common fragmentation channels, corresponding to multiple neutral losses of ammonia (17 Da), hydrogen cyanamide, $NCNH_2$ (42 Da) and hydrogen dicyanamide $N(CN)_2H$ (67 Da).

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Scheme 1. Tandem MS analysis of major species constituting the precipitate formed during the reaction of DCA ILs with HNO_3 (Figures 1 and 2). Common fragmentation channels include multiple neutral losses of ammonia (17 Da), hydrogen cyanamide, $NCNH_2$ (42 Da) and hydrogen dicyanamide $N(CN)_2H$ (67 Da).

The similarity of fragmentation channels suggests structural homology of the detected species. Based on the fragmentation patterns in Scheme 1, the peak at *m/z* 127 appears to be an essential structural building block for most of the compounds. From high-resolution MS analysis the only chemical formula associated with this signal was calculated to be $C_3N_6H_7^+$. We propose that the identity of this species is protonated melamine based on the reported tandem mass spectra for this compound, which contain fragments at *m/z* 110, 85, and 68.[9] We confirmed this assignment by a reference experiment on authentic melamine.

Given the high temperature during hypergolic ignition, we propose that the formation of melamine in our experiments proceeds via heat-induced reaction of DCA with ammonia to yield cyanoguanidine,[10] which on further heating polymerizes into melamine,[11] as shown in Scheme 2. Ammonia in our experiments presumably originates from thermal decomposition of IL cations. Thus, the elimination of ammonia from N-containing cyclic cations of DCA ILs has been reported at 300 °C.[12] Alternatively, ammonia can be formed during the reaction between DCA and nitric acid via dinitrobiuret intermediate.[6] The latter undergoes thermal decomposition into HNCO,[13] which is then hydrolyzed to yield NH_3 and CO_2.[14] The signals at *m/z* 127, 236, and 345 in Figure 1a are separated from each other by 109 Da, indicating the polymerization of melamine (Scheme 2). The "dimer" is commonly referred to as melam (*m.w.* 235) and is known to be a product of thermal condensation of melamine.[15] Upon heating, melam is known to lose ammonia to form melem (*m.w.* 218).[16] Melem can also be generated by thermal treatment of other less condensed C-N-H compounds, such as melamine, dicyandiamide, ammonium dicyanamide or cyanamide.[16, 17] As follows from its fragmentation pattern (Scheme 1), the species at *m/z* 169 consists of melamine with cyanamide attached, which can be an intermediate during the polymerization of melamine to melam and melem (Scheme 2, *m.w.* 168). The species at *m/z* 152 is formed from *m/z* 169 by the loss of ammonia (Scheme 1). It is probably the only species out of those detected in which the *s*-triazine ring structure is broken (Scheme 2, *m.w.* 151). The signals described above were detected for all the DCA ILs tested in this study (see Experimental).

Most of the peaks in Figure 1a are accompanied by signals with a shift of one mass unit. These adjacent peaks have the same nominal mass but much stronger relative intensities than those expected from ^{13}C isotopes (e.g., see the inset in Figure 1a for a doublet *m/z* 127 – 128). As derived from high-accuracy mass measurements, these signals arise from the substitution of NH_2 functionality with OH. For example, the corresponding substituent for melamine is referred to as ammeline (Scheme 2, *m.w.* 127) and is readily produced from melamine by hydrolysis in strong acid.[18] The presence of OH group was supported by the MS/MS analysis that revealed the neutral loss of 18 mass units (water). Upon the hydrolysis of triazine compounds to corresponding hydroxyls, the latter become visible in negative ion detection mode via deprotonation of OH groups (Figure 1b). For example, the peak at *m/z* 126 corresponds to deprotonated ammeline and the peak at *m/z* 218 to hydroxy-substituted melem. The latter dominates the spectrum in negative ion mode probably because melem is most predisposed to hydrolysis to its hydroxy-substituted version.

Thermal decomposition into melamine-like cyclic azines has been reported for a number of energetic materials.[19, 20] For example, the formation of melamine, melem, melon, and ammeline has been observed from dicyandiamide, diaminoglyoxime and diaminofurazan when heated at a rate of 100°C/*s* at a pressure of up to 1000 psi of Ar.[19] DCA ILs with N-containing cations have

recently been reported to condense into triazine rings at ~ 500 °C, which upon further heating (up to ~ 1000 °C) gave rise to dense nitrogen-doped carbon materials.[12, 21] While the high temperature accompanying hypergolic ignition is apparently responsible for the decomposition of ILs, it is not the only factor to be considered in our experiments. Thus, the rapid polymerization observed can also be caused by the low pH arising from the high concentration of nitric acid.
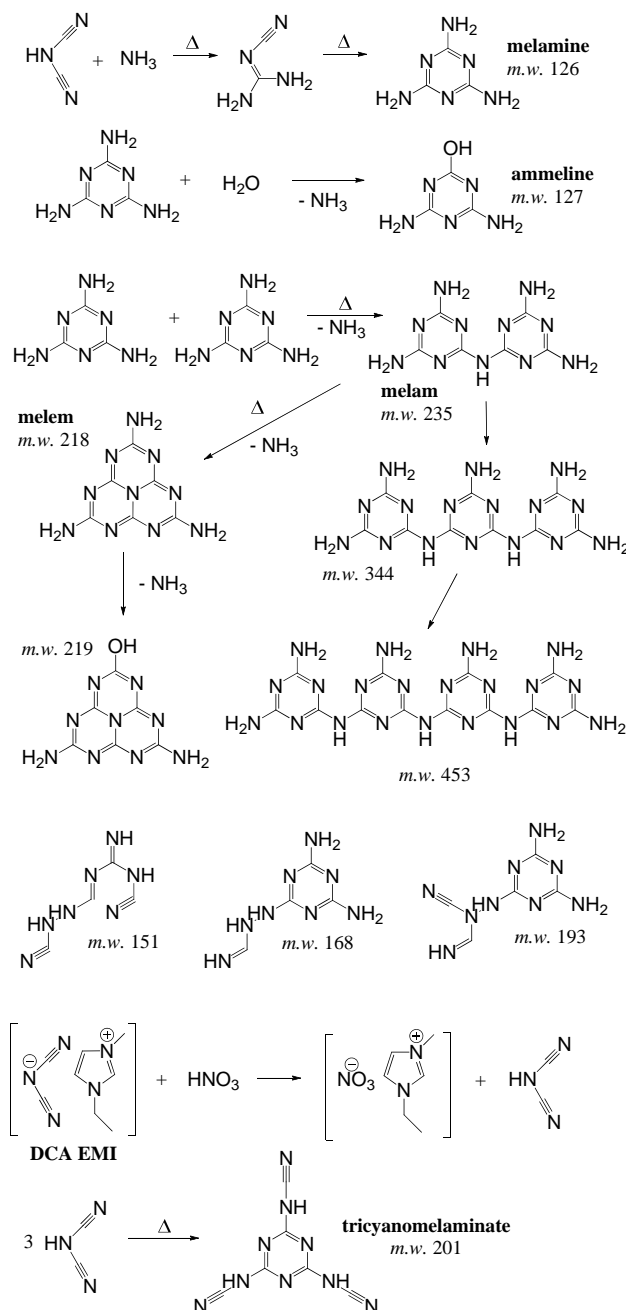
Scheme 2. Proposed structures and mechanisms for the formation of the species observed in the reaction between dicyanamide ILs and nitric acid.

To explore the reactivity of DCA ILs with nitric acid a set of experiments was performed in which various DCA ILs were mixed in bulk with aqueous HNO_3 (10% *vol*). Due to the lower concentration of components, the reaction was much slower and no

ignition occurred. Still, we observed vigorous bubbling, indicating release of volatile products, and finally, after ~ 1 min, formation of a precipitate. Solid- and liquid-phase products were isolated by centrifuging and then analyzed separately. Solution phase was diluted in water ($\times 10^{-3}$) and then analyzed using direct-infusion ESI-MS. Figure 2a shows the resulting mass spectrum in negative ion detection mode when the DCA IL with the 1-ethyl-3-methylimidazolium (EMI) cation was used.
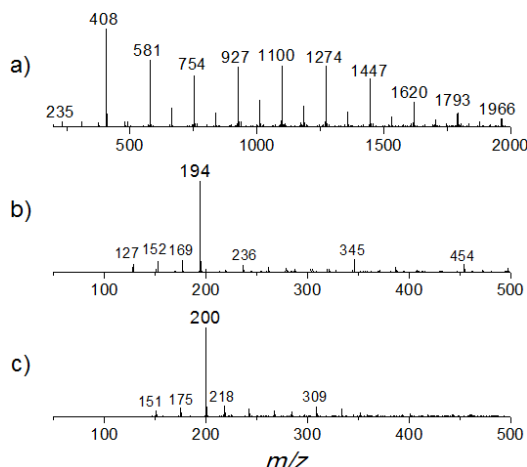
Figure 2. Products of the reaction between 1-ethyl-3-methylimidazolium dicyanamide and aqueous nitric acid (10% *vol*) analyzed by ESI-MS: (a) solution phase (diluted 10^3 times in pure water) analyzed in negative ion detection mode; (b) and (c) are the MS of the precipitate (dissolved in ammonium hydroxide) analyzed in positive and negative ion detection modes, respectively.

The spectrum is dominated by clusters with the molecular composition of $[EMI^+]_{n-1}[NO_3^-]_n$ (n ≥ 1), pointing at the formation of $[EMI^+][NO_3^-]$ salt during the reaction. It can be concluded from this observation that HNO_3 and $[EMI^+][DCA^-]$ IL undergo ion exchange – EMI^+ pairs with NO_3^- to form water-soluble salt, while DCA^- interacts with protons to yield the precipitate (Scheme 2). Another important conclusion from Figure 2a is that EMI^+ cations mostly remain intact, pointing at a relatively low temperature during the reaction.[22]

The precipitate was washed in water and then dissolved in ammonium hydroxide (10% *vol*) for ESI-MS analysis. Analogous to the precipitate formed under the conditions of hypergolic ignition (Figure 1), the precipitate from the model reaction between DCA ILs and aqueous HNO_3 also reveals the presence of melamine and its oligomers (Figures 2b and 2c), including the one at *m/z* 454 (*m.w.* 453, Scheme 2). However, as follows from the mass spectrum, the major polymerization channels are clearly different. For all the ILs tested, mass spectra of precipitate are dominated by the signal at *m/z* 194 in positive ion mode and *m/z* 200 in negative. Based on tandem MS analysis (Scheme 1), the compound at *m/z* 194 was found to consist of dicyanamide attached to melamine (Scheme 2, *m.w.* 193). This observation points possibly to a lower-energy polymerization pathway of melamine than that associated with the intermediate at *m/z* 169 observed under hypergolic conditions (Scheme 2, *m.w.* 168). The signal at *m/z* 200 was identified as a dicyanamide trimer, known as tricyanomelaminate (Schemes 1 and 2). Its synthesis has been reported via thermally induced (~ 300 °C) trimerization of alkali DCA salts (M = Li, Na, K and Rb).[23] In our experiments, each tricyanomelaminate molecule originates from three DCA anions and

three protons donated by nitric acid, which is in full agreement with the ion exchange reaction mechanism proposed above.

We suggest that the formation of tricyanomelaminate becomes a dominant polymerization channel at lower temperatures. At lower temperatures, considerably less ammonia is eliminated from IL during the reaction, which decelerates the concurrent polymerization of DCA into melamine (Scheme 2).

In summary, we found that various *s*-triazine compounds are generated during the ignition of hypergolic dicyanamide ionic liquids with nitric acid, among which we identified melamine and its oligomers, e.g. melam and melem. A mechanism was proposed for the formation of the major polymers via thermal decomposition of DCA ILs, mediated by nitric acid, which competes with the hypergolic oxidation mechanism. While our discovery imposes certain implications on the use of DCA ILs as bipropellant fuels, it demonstrates an interesting approach to facile synthesis of cyclic azines, which constitute the forefront of modern carbon nitride chemistry.[24] Condensation is readily achieved by mixing DCA IL with HNO_3 at ambient temperature and pressure. The concomitant ignition can be avoided during the synthesis simply by sufficient dilution of the oxidizer in water prior to reaction.

Experimental Section

Hypergolic reaction was initiated when a drop of WFNA introduced from a gastight syringe fell into a small cuvette containing a small amount (ca. 0.5 mL) of IL fuel. Liquid was decanted, and the residue was centrifuged and washed in water 30 times. The recovered precipitate was dissolved in ammonium hydroxide and then directly analyzed by ESI-MS in both positive and negative ion detection modes. Most MS and MS^n (n ≥ 2) analyses were performed on a Finnigan LCQ Classic mass spectrometer (Thermo, San Jose, CA, USA). Since the efficiency of collision-induced dissociation in LCQ is limited by the need to trap fragment ions, for some low molecular weight species (*m/z* < 200) complementary MS^2 analysis was carried out using a quadrupole time-of-flight instrument (QTOF, Waters, Manchester, UK) to provide more abundant fragmentation. High-resolution mass measurements were done on an Orbitrap Exactive mass spectrometer (Thermo, San Jose, CA, USA). DCA ILs with the following cations were purchased: 1-butyl-1-methyl-pyrrolidinium, N-butyl-3-methylpyridinium (EMD Chemicals Inc., Darmstadt, Germany), 1-ethyl-3-methylimidazolium and 1-butyl-3-methyl-imidazolium (Fluka Analytical, Steinheim, Germany). Nitric acid was obtained from Fisher Scientific (Hampton, NH, USA) and melamine from Fluka.

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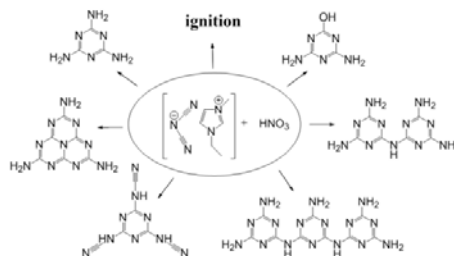
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The reaction of dicyanamide ionic liquids with nitric acid results in hypergolic ignition and the formation of a stable precipitate. The precipitate consists of cyclic triazines, including melamine and its polymers, such as melam and melem. Our study provides mechanistic insight into the chemistry of hypergolic ionic liquids and introduces a novel approach to the synthesis of cyclic azines.